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# STRUCTURAL ASSESSMENT OF MONODISPERSE CERAMIC COMPOSITES

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Methods for determining the dependence of the average distance between particles in monodisperse composites are analyzed. A more accurate method of determining the average distance between particles in disperse systems with an indication of the coordination number taking account of the volume density, connectedness, and degree of compaction of the system on the basis of the corpuscular and percolation models is proposed. A comparison of experiments and the calculations performed with the more accurate method show good agreement. The method is applicable for composite, porous, and colloidal systems.

***Key words:*** disperse system, structure, volume density, interparticle distance, coordination number, corpuscular and percolation models, compaction, composite materials, porous and colloidal systems.

The structure of composite and porous materials largely determines their physical characteristics [1 – 5]. The basic structural parameters of these systems are particle size and interparticle contacts, character and density distribution of the solid phase in the disperse medium (matrix).

The properties of the macro- and microscopically inhomogeneous powder materials are described with different fractal [1, 2] and structural-percolation [3 – 5] models.

Apparently, fractal models are desirable only for nanomaterials, composites with three (or more) fractions, and self-organizing (in which the elements of the universe's creator are clearly evident) systems. Structural and percolation models are physically more rigorous for porous and composite materials consisting of particles larger than 1 μm. For example, it is convenient to use the structural model presented in [4, 5] for permeable and composite monodisperse systems, where indices such as the following are used: $D$ — the average particle size in the system (material), $P$ — porosity of the system, $V$ — the relative volume packing density of the particles in the system, $d$ — size of the interparticle contacts. The missing parameters are easily determined from the engineering expressions: $Z$ — average coordination number; $S_o$ — specific surface area; $r$ — average radius; $\xi$ — the sinuosity of the capillaries (for porous materials); $N_c$ — number of contacts; and, $S_{oc}$ — area of the interparticle contacts per unit volume. Here we start from the fact that unit volume of the material being modeled contains $N = 6(1 - P)/(\pi D^3)$ particles:

$$V = 1 - P = (1 - 2/Z)^2/[8(1.077 - 1/Z - Z^{-1.16})(0.5 - h/D)^3]; \quad (1)$$

$$h/D = h_o/D - 4(h_o/D)^2(1.5 - h_o/D)/3, \quad h_o/D = [1 - (1 - d^2/D^2)^{0.5}]/2; \quad (2)$$

$$S_o = 6(1 - P)\{1 - Z[h_o/D - d/D(h_o - h)/D]\}/D; \quad (3)$$

$$\xi = 2/\{P[1 - (1 - 2h/D)\ln P]/v)\}; \quad (4)$$

$$r = 2P[(6/Z)^{0.2}/\xi^{0.5}]/S_o; \quad (5)$$

$$N_c = 3Z(1 - P)/(\pi D^3), \; S_{oc} = 3Z(1 - P)d^2/(4D^3), \quad (6)$$

where $h$ is the interparticle contact height; $h/D$ is the normal deformation of the particles; $v$ is the shape factor, equal to 0.5 for spherical particles; $h_o$ is the height of the spherical segment per contact.

Calculations preformed using the expressions (1) and (2) with $d = 0$ agree with the experimental data. Thus, for $Z = 2.64$ (percolation threshold) we obtain $V = 0.157$ while for $Z = 7.3$ we obtain the random packing density of the filler $V_r = 0.63$.

The structure of porous and composite monodispersed materials is often evaluated only according to the values of the average particle size of the disperse phase $D$, particle number density $N$ (or particle volume density in a disperse medium (system) $V = \pi D^3 N/6$) and average distance $L$ be-

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tween the centers of the particles [6 – 10], which complicates the optimization of the structure of these systems.

The simplest approach to determining the average interparticle distance in a model of spherical particles is presented in [6]. If the relative volume $V$ of the particles with diameter $D$ in the system is known, then the following computational expression is obtained:

$$D/L = (V/(\pi/6))^{1/3}. \quad (7)$$

If the number $N$ of spherical particles per unit volume of the composite is known, then the calculation simplifies even more: $L = 1/N^{1/3}$.

It follows from the expression (7) that for $V = V_{cr} = 0.157$ we obtain $D/L = 0.6693$, for $V = V_r = 0.63$ we have $D/L = 1.0636$, and only for $V = 0.5235$ the ratio will be $D/L = 1.000$ ($V_{cr}$ is the critical volume density of the particles). In the experimental data, for example [5, 11], $D/L = 1.000$ in all cases for these values of $V$, i.e., the assessment obtained for the structure of the material is too arbitrary.

Attempts to refine the assessment of the structure of monodisperse systems in obtaining composites with prescribed properties and optimizing the structure of materials are examined in [7 – 10]. Thus, in [7 – 9] analysis of the structure of tribotechnical composite materials was used to develop durable powder materials with high antifriction properties. In [10] the problem of assessing the structure of monodisperse systems was analyzed from the standpoint of astrophysics.

It is shown in [8] that the average distance between the centers of neighboring particles for a random uniform distribution of noninteracting particles, determined according to [10] as $L = \Gamma(4/3)(4\pi N^{-1/3}) = 0.554N^{-1/3}$, where $N$ is the number density of particles, $\Gamma(4/3)$ is the value of the gamma function for argument $4/3$, as well as the ordinarily used estimate of the average distance according to the expression (1) and a similar expression for hexagonal packing $L = D = 1.225N^{-1/3}$ are too rough. For this reason the following interpolation relation was proposed:

$$L(V) = a(V)N_o^{1/3} = [0.56V^{1/3} + 1/(2.24V^{1/3})]\,D, \quad (8)$$

where the function $a(V)$ assumes the value 0.5554 as $V \to 0$ and 1.1225 at $V = 0.74$.

The expression (8) was obtained by computer modeling. However, this algorithm is applicable only to density $V = 0.45$, showing its limited nature, since the actually achievable density of random packing of noninteracting spherical particles $V_r$ is 0.63 [11].

In [10] the parameter $L$ is calculated by a probabilistic method

$$L = 1.19D/V^{1/3}, \quad (9)$$

where $\Gamma(7/3) = 1/19$ is the value of the gamma function for argument $7/3$.

The use of the Poisson distribution makes the estimate of the parameter $L$ less reliable. For example, for random packing of a filler with $V_r = 0.63$ the average distance between the centers of the spherical particles is equal to their diameter $D$. According to the expression (9) we obtain $D/L = 0.7204$. For critical filler density $V_{cr} = 0.157$ we have $D/L = 0.4534$ and for $V = 0.5$ the ratio $D/L = 0.6667$. This also does not correspond to real systems [11].

The foregoing analysis shows that a more accurate method of evaluating the parameter $L$ in composite systems must be developed.

In the present work a more rigorous method of estimating the parameter $L$ in heterogeneous systems is presented. This method is based on the assumption that it is not sufficient to prescribe a single parameter $L$ as the structural characteristic of a system. It is also necessary to give the coordination number $Z$.

Indeed, for volume density $V$ of the disperse phase less than the random packing density $V_r$ the parameter $L$ can depend on the volume density of the disperse phase and on the average coordination number $Z$ (number of particles with which a central particle is in contact in the first coordination zone), and for composites also on fabrication technology, for example, on the thickness of the cover layer pre-deposited on a particle (if it consists of the matrix phase). Thus, in calculating the relative volume of the solid phase of the system using the expression (1) and (2) we obtain different values of $V$ for a heterogeneous system for $L = D$: $V = 0.63$ ($Z = 7.3$); $V = 0.4$ ($Z = 4$); $V = 0.157$ ($Z = 2.64$) with $h/D = 0$.

For volume density $V$ of the disperse phase greater than the random packing density $V_r$ the dependence of the parameter $L$ on the porosity is also not single-valued. The parameter $L$ depends on the average size $d$ of the interparticle contacts (or the normal deformation $h/D$ at the center of the contact $h/D$), which for prescribed concentration of the solid phase depend on, in turn, the average coordination number $Z$. For definite types of vibratory compaction and $d$ close to zero (the parameter $L$ remains practically unchanged and equal to the average diameter of the particles $D$) the relative density of the system can be increased to $V \sim 0.74$ only as a result of an increase of the coordination number $Z$.

From the standpoint of percolation theory low-concentration systems with density $V_{aux} < V_{cr} = 0.157$ ($Z < 2.64$) are unbound and hence indeterminate ($V_{aux}$ is the random packing of auxiliary spheres with volume density of the particles with critical coordination number $Z = 2.64$ and $V_{aux} = V_{cr} = 0.157$).

To increase the determinateness of the systems and to take account of the particle size and the type of system formed, we shall employ a system model in the form of quasipacking of auxiliary spheres with diameter $L$. It is convenient to take as the base packing a random packing of auxiliary spheres with relative particle packing density $V_{aux}$ with critical coordination number $Z = 2.64$ and $V_{aux} = V_{cr} = 0.157$. Then the auxiliary spheres form a minimally bound

(statistically determinate) system along which conduction (of heat or electricity) is possible from the stand point of percolation theory. Since the average size $D$ of the particles is less than $L$, a partially determinate system of randomly distributed noninteracting particles (each particle of system can be found anywhere inside the corresponding auxiliary sphere with diameter $L$ — on average at its center) is obtained. From the relation $V_{aux} = \pi NL^3/6 = 0.157$ with $Z = 2.64$ and $V = \pi ND^3/6$ we have

$$L = 0.5395DV^{-1/3} = 0.6693N^{-1/3} \quad \text{for } Z = 2.64 \text{ and } V < 0.157. \tag{10}$$

The shortest average distance between the boundary of the particles $\delta = L - D$ is given by the relation

$$\delta = (0.5395V^{-1/3} - 1)\, D = L\,[1 - (V/0.157)^{1/3}] \quad \text{for } Z = 2.64 \text{ and } V < 0.157. \tag{11}$$

The expressions (10) and (11) are also applicable for gaseous or liquid finely disperse (colloidal) and course systems.

For $V_{aux} = 0.157$ with a cover layer of thickness $\delta_{lay}$ pre-deposited on the particles the critical volume density of the disperse phase $V'_{cr}$ does not reach the theoretical critical value equal to 0.157 (see Fig. 1, dashed line):

$$V'_{cr} = 0.157(1 - \delta_{lay}/L)^3. \tag{12}$$

It follows from the expressions (10) – (12) that for $V \le 0.157$ the system is determinate only if the average size $D$ of the particles or $(D + \delta_{lay})$ equals $L$ and $V_{aux} = V_{cr} = 0.157$.

For $V \ge 0.157$ the system can be assumed to be statistically determinate, i.e., consisting of randomly and uniformly distributed contacting particles. The value of $L$ is constant. It can be greater than $D$ (if $\delta_{lay} > 1$, i.e., the system being analyzed is of the matrix type), equal to $D$ ($\delta = 0$, $h/D = 0$), or less than $D$ (if $h/D > 0$). The coordination number is calculated from the expression (1). For $Z = 7.3$ and $V = V_r$ the contacting particles form a rigidly bonded system and there is no longer any need to use a model of a system in the form of quasi-packing of auxiliary spheres with diameter $L$.

However, by analogy with the approach to loose packing it is convenient to examine the system being analyzed for $V_r \ge V \ge 0.157$ as partially determinate, using the model of a system in the form of random close packing of auxiliary spheres with diameter $L$ with constant $Z = 7.3$. In this case only auxiliary spheres form a rigid bounded (determinate) system. The value of $L$ is also greater than $D$. The density of the system determines the shortest average distance $\delta$ between the boundaries of the particles:

$$L = 0.8573DV^{-1/3} = [3.78/(\pi N)]^{1/3} \quad \text{for } Z = 7.3 \text{ and } 0.157 \le V_{aux} \le V_r; \tag{13}$$

$$\delta = (0.8573V^{-1/3} - 1)\, D = L\,[1 - (V/0.63)^{1/3}] \quad \text{for } Z = 7.3 \text{ and } 0.157 \le V_{aux} \le V_r. \tag{14}$$

The expressions (13) and (14) make the structural assessment of inhomogeneous systems more rigorous.

For $V = V_r$ (in the presence or absence of a cover layer of thickness $\delta_{lay}$ pre-deposited on the particles) the particles of the solid phase form a rigidly bound (determinate) system. The value of $L$ can also be greater than $D$ if the system being analyzed is of the matrix type (for example, matrix composite). The shortest average distance $\delta$ between the boundaries of the particles in such a system is determined by the thickness $\delta_{lay}$ of the cover layer pre-deposited on the particles.

For $V_{aux} = V_r$ and thickness $\delta_{lay}$ of the cover layer pre-deposited on the particles the volume density of the random packing of the particles with a cover layer of a disperse phase $V'_r = V_r(1 - \delta_{lay}/L)^3$ does not reach the value $V_r$ (see Fig. 1, dashed line).

Subsequent packing (for example, vibratory compaction) of a disperse system, i.e., for $V \ge V_r$, does not increase the statistical determinateness, with the exception of the extreme case ($V = 1$, $Z = 14$ [11]) where the expression (1) gives $L/D = 1.0928$ (see Fig. 1). Values of $L$ equal to or less than $D$ and the porosity of the system are determined not only by the coordination number but also by the size of the interparticle contacts. Thus, the statistical determinateness of the system can be increased only if aside from $L$ and $Z$ the average size of the interparticle contacts (or average normal deformation of the particles in the contact zone) is given.

In the present model this can be taken into account by supplementing the expression (1) for porosity $P < 0.37$ by an approximate linear dependence on $Z$ of the average normal deformation of the particles in the contact zone (we neglect the large difference in the sizes in the eight primary and six secondary contacts between the particles):

$$h/D = (Z - 7.3)/158; \quad 7.3 \le Z \le 0.14. \tag{15}$$

The maximum value $Z = 14$, adopted on the basis of the experimental data for compact material [11], substituted into the expressions (15) and (1) gives the relative density $V = 1$.

Let us compare the value $D/L = 1.0928$ obtained from the expression (1) for $V = 1$ with the results following from the model of nonporous powder materials ($Z = 14$), based on elementary semi-regular polyhedral in the form of a truncated octahedron (bounded by eight regular hexagons and six squares). The polyhedral chosen completely fill the space. A coordination number of 14 and the average number of vertices in its faces, equal to 5.143, correspond to the experimental data [11].

Nonporous material is obtained in this model for $Z = 14$ with average deformation $h/D = 0.04244$ and correspondingly the contact size $d = 0.5657D$ according to the expression (1). It follows from the equality of the volumes of a semi-regular polyhedron and a sphere that for $P = 0$ we have $h/D = 0.0395$ or $D/L = 1.0858$. The values obtained are quite close, which supports our approach.

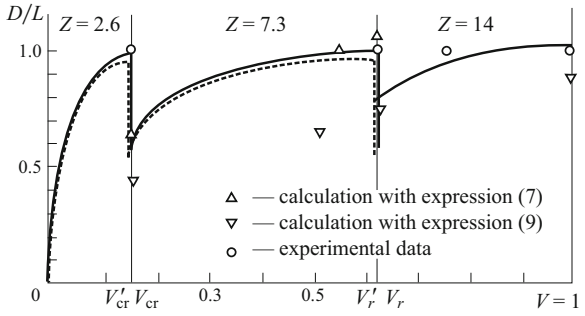


**Fig. 1.** Relative average distance between particles $D/L$ in a disperse system versus the volume density $V$ of the particles in this system.

Similarly to the approach used to obtain the computational expressions (13) and (14) for $Z < 7.3$ with system porosity less than the random packing the average distance $L$ is best determined on the basis of the maximum coordination number $Z = 14$.

To simplify the computational expressions we shall use the least-squares method for $L$ with reference values of the relative particle packing density in the system $V_{Z=7.3} = 0.63$, $L_{Z=14} = 1.24D$; $V_{Z=8} = 0.652$, $L_{Z=14} = 1.18D$; $V_{Z=12} = 0.7405$, $L_{Z=14} = 1.0905D$; $V_{Z=14} = 1$, $L_{Z=14} = 0.9151$. Since the average distance should not depend on the contact size (we are considering in each case a region where 14 particles are in contact with one particle), the contacts were assumed to point contacts (with the exception of the values for $Z = 14$). Thus, for $V_{Z=12} = 0.7405$ (closest hexagonal packing) we have 12 direct point contacts ($L = D$) and two particles, located from the chosen particle at distance $L = 1.6337D$ (equal to twice the height of a regular tetrahedron). Then the average arithmetic distance is $L_{Z=12} = (12 + 2 \times 1.6337)/14 = 1.0905$. We obtain the result

$$L = (2.25 - 1.335^{0.5})\, D \quad (\text{for } Z = 14), \quad 0.63 < V < 1 \quad (L \geq 0.9151D); \tag{16}$$

$$h = (0.6675V^{0.5} - 0.625)\, D \quad (\text{for } Z = 14), \quad 0.63 < V < 1 \quad (h \leq 0.04244D). \tag{17}$$

Figure 1 shows the computational results for the average distance $L$ between the centers of the particles according to the expressions (10), (13), and (16). The figure also indicates the experimental values $V_{cr} = 0.157$ for $Z = 2.64$, $V_{cr} = 0.63$ for $Z = 7.3$, and $V = 0.63$ for $Z = 12$ (packing or vibratory compaction), obtained with different volume density of the filler for the same value of $D/L = 1$. In addition, the figure shows the results of the calculation of $L$ from the expressions (7) and (9). The figure confirms the methods of [6 – 10], i.e., structural assessments of the monodisperse systems using only the average interparticle distance, are incorrect.

## CONCLUSIONS

It has been shown that the conventional method used to assess the structure of monodisperse systems by means of the average interparticle distance is incorrect. This method was refined by indicating the average coordination number of a monodisperse powder system as well as by taking account of the connectedness of the system ($V < V_{cr}$) based on the corpuscular model and percolation theory.

A refined method of determining the average distance between particles in dense disperse systems for $V > V_r$ taking account of the coordination number and the average size of the interparticle contacts was proposed.

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